



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Group Art Unit: 1204
Examiner: Mr. Alan M. Siegel

#28
Sweet
4/30/98

1573

In re PATENT APPLICATION of:

Applicants : Pascal PENNETREAU et al.)

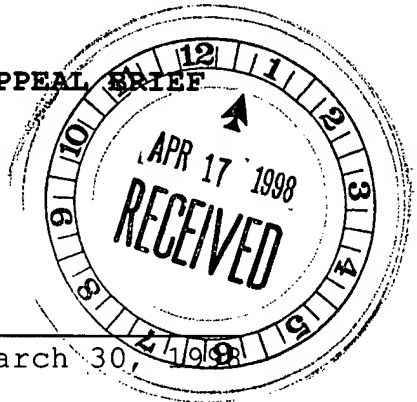
Application No.: 08/549,322)

Filed : October 27, 1995)

For : PROCESS FOR THE
PREPARATION OF 1-CHLORO-
FLUOROETHANE AND/OR
1,1-DIFLUOROETHANE)

Attorney Docket: SLVAY 0829)

APPEAL BRIEF



March 30, 1998

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

Pursuant to 37 CFR 1.192(a), applicants submit herewith their Appeal Brief in triplicate. A Notice of Appeal was timely filed in the U.S. Patent and Trademark Office on January 29, 1998.

The fee required by 37 CFR 1.17(f) is enclosed.

(1) Real Party in Interest

The identified patent application and the invention disclosed and claimed therein are assigned to Solvay (Société Anonyme) by an assignment recorded on August 2, 1994 at microfilm Reel 7100, Frames 267-68.

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The identified patent application and the invention

(2) Related Appeals and Interferences

No other appeals or interferences which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal are known to applicants' legal representative.

(3) Status of Claims

Claims 1 to 29 are pending, and present in this appeal.

(4) Status of Amendments

An Amendment was filed on December 29, 1997. The Advisory Action dated January 26, 1998 states that upon filing of an Appeal, this Amendment will be entered.

(5) Summary of Invention

The present invention is directed to a process for the manufacture of 1-chloro-1-fluoroethane, 1,1-difluoroethane, or mixtures thereof, with reduced formation of heavy halogen-containing side products. The process comprises reacting hydrogen fluoride with vinyl chloride in the liquid phase, specifically in an organic solvent consisting of at least one saturated halogen-containing hydrocarbon. The introduction of the vinyl chloride and the hydrogen fluoride may be controlled

so that, at all times, the vinyl chloride content is less than 15% and the hydrogen fluoride content is less than 30%, both compared to the weight of the reaction mixture. The molar ratio between hydrogen fluoride and vinyl chloride is preferably at least 1 and does not exceed 20.

The saturated halogen-containing hydrocarbon may be selected from chloro-, fluoro-, or chlorofluoro hydrocarbons containing from 1 to 8 carbon atoms.

The reaction may be carried out in the presence of a hydrofluorination catalyst selected from the group consisting of derivatives of metals of Groups IIIa, IVa, IVb, Va, Vb, and VIb of the Periodic Table of the Elements, and their mixtures. The reaction is preferably performed at a temperature of at least 40°C and not exceeding 130°C, and at a pressure of at least 2 bar and not exceeding 50 bar.

The desired product may be continuously withdrawn from the reaction mixture. For example, if the desired product is 1,1-difluoroethane it may be continuously withdrawn in gaseous form.

(6) Issues

The sole issue is whether the subject matter of the rejected claims would have been obvious to a person of ordinary

skill in the art, at the time applicants made their invention, in view of the disclosures of U.S. Patent No. 5,008,474 to Walraevens considered together with published International Application WO 89/12614 to Rao, and a publication by Lovelace.

(7) Grouping of Claims

For the reasons discussed below, applicants respectfully submit that their claims do not stand nor fall together.

(8) Arguments

The Examiner asserts that:

The use of vinyl chloride and vinylidene chloride in hydrofluorination processes in general is so well known that the use of one would immediately suggest the use of the other to one of ordinary skill in the art.

Applicants respectfully submit that the above-quoted statement is an unsupported statement of fact. Pursuant to 37 CFR 1.107(b), applicants respectfully call upon the Examiner to submit his own Declaration or Affidavit in support of the above-quoted statement.

The present invention provides an improved process for making 1-chloro-1-fluoroethane and/or 1,1-difluoroethane from vinyl chloride and hydrogen fluoride while, at the same time avoiding the unwanted formation of heavy halogen-containing side products as described in the specification at page 2, lines 23 to 31, and set forth in claims 1 and 21. Applicants respectfully submit that this important feature of the invention is neither disclosed nor suggested by any of the references.

The Examiner has alleged that no objective evidence has been submitted that the problem solved by the invention exists and is solved by the present invention. The Board's attention is respectfully directed to comparative Examples 1, 2, and 4 at pages 9 to 11 of the present specification. These Examples are clearly **evidence** of the formation of large amounts of heavy by-products in the reaction between vinyl chloride and HF. As the Board will note, from 25 to 46% of the vinyl chloride is converted in these conditions into heavy side products.

Furthermore, Examples 3 and 5 to 19, according to the invention, are further **evidence** that the present invention limits the formation of heavy-by-products to reasonable amounts. In these Examples a maximum of 13% of vinyl chloride is converted into heavy side products (see Example 10).

Clearly this means that the formation of heavy side products is reduced by at least half over the previously known process for preparing 1-chloro-1-fluoroethane and/or 1,1-difluoroethane starting from vinyl chloride. In this respect, the Examiner is respectfully requested to compare the worst Example according to the present invention (Example 10) with the "best" comparative Example (Example 4). Applicants therefore respectfully submit that there is **evidence of record** that the problem solved by the present invention exists and is solved "by the present invention."

The Examiner has also alleged that there is no objective evidence that "the analogous starting material of the primary reference" would behave differently in "the same chemical process." The tests reported at pages 1 and 2 of the Declaration under 37 CFR 1.132 filed March 24, 1995 (Appendix 2 to the present Brief) are clearly **evidence** that vinylidene chloride and vinyl chloride behave differently when reacted with HF in similar conditions, either in the presence or absence of a catalyst. Moreover, the replacement of the starting material in a given chemical process inevitably modifies the process. It is thus not possible to test vinyl chloride and vinylidene chloride in the "same" chemical process. It is therefore clear that objective evidence has

been submitted that the "analogous starting material of the primary reference" does behave differently in the "same" chemical process.

The Examiner has alleged "that the instantly claimed process is only involved with the simple reaction between HF and vinyl chloride to produce 1-chloro-1-fluoroethane and/or 1,1-difluoroethane." It is unclear what thermodynamic and kinetic information (e.g. the chemical equilibria involved) the Examiner relies upon to support his conclusion with respect to "the simple reaction" The Examiner is therefore invited to submit his Declaration in accordance with 37 CFR 1.107(b) in order that he may share his information with the applicants. In the absence of the Examiner's Declaration, there is absolutely no **evidence** of record that the reaction between HF and vinyl chloride to produce 1-chloro-1-fluoroethane and/or 1,1-difluoroethane is a "simple reaction."

As to the alleged consistency of the reaction results, applicants respectfully submit that quite different chemical equilibria are involved in the two processes. In particular, in the presently claimed process, the parallel reactions of vinyl chloride and 1-chloro-1-fluoroethane with ClH produced, leading to 1,1-dichloroethane, are far more important than similar reactions of vinylidene chloride and 1,1-dichloro-1-

fluoroethane with ClH , which would lead to 1,1,1-trichloroethane in the Walraevens process.

Walraevens describes a process for the manufacture of 1-chloro-1,1-difluoroethane from vinylidene chloride by reaction with hydrogen fluoride (column 1, lines 14 to 16). By-products of this reaction include 1,1,1-trifluoroethane as well as 1,1-dichloro-1-fluoroethane, vinylidene chloride, and 1,1,1-trichloroethane (see column 4, lines 5 to 8). The entire disclosure of Walraevens is concerned with a process using **vinylidene chloride** as the starting material. There is no description or suggestion in Walraevens that any other starting material could be used, with a reasonable likelihood of success. In sharp contrast to Walraevens et al., the present process uses a different starting material, namely vinyl chloride ($\text{CH}_2=\text{CHCl}$) instead of vinylidene chloride ($\text{CH}_2=\text{CCl}_2$), which obviously lead to different products.

The process set forth in claim 11 above, further differs from the disclosure of Walraevens et al. in the use of a different organic solvent, namely 1,3-dichloro-1-fluorobutane. In sharp contrast, the Walraevens disclosure requires a liquid medium containing 1,1-dichloro-1-fluoroethane.

As to the "analogy" of the starting materials, beyond the structural analogy between vinyl chloride and vinylidene

chloride, applicants note that these materials have well known **very different** reactivities. Vinyl chloride is far more reactive than vinylidene chloride, and thus has a far greater tendency than vinylidene chloride to form "heavies" by oligomerization.

Rao discloses the structural analogy between vinyl chloride and vinylidene chloride. **Rao contains no examples using vinyl chloride or vinylidene chloride as a starting material.** No conclusion concerning their respective behavior in the Rao process can thus be gleaned from the published application and, fortiori, no conclusion concerning the alleged analogy between these two compounds can be reached.

At page 4 of the Official Action the Examiner states: "[T]he instant rejection is not predicated on the assumption that vinyl chloride and vinylidene chloride are identical reactants but only that there would have been a reasonable expectation that **some useful analogous product** would be obtained." The present invention does not contain claims to "some useful analogous product," but provides a highly efficient process for the preparation of 1-chloro-1-fluoroethane and/or 1,1-difluoroethane starting from vinyl chloride and, at the same time, avoiding the unwanted formation of heavy halogen-containing side products. The Examiner's

reasoning set forth in the last paragraph at page 2 of the Official Action is a clear statement of the improper "obvious-to-try" standard. There is, in fact, no suggestion in Walraevens that any other starting material could be used in place of vinylidene chloride with a reasonable likelihood of success in avoiding the unwanted formation of heavy halogen-containing side products. This is particularly true when the starting material is vinyl chloride which, as **evidenced** in the Declaration filed March 24, 1995, is more highly reactive than vinylidene chloride and thus has a far higher tendency to form heavy halogen-containing side products than vinylidene chloride (see the paragraph spanning pages 2 and 3 of the Declaration). Applicants respectfully submit that the Examiner has totally disregarded the **evidence** of record concerning the different behavior of vinyl chloride and vinylidene chloride. Applicants respectfully submit that the Examiner's argument about the motivation to use vinyl chloride instead of vinylidene chloride is based on pure speculation and unfounded assumptions. In particular, it is unclear why a person of ordinary skill in the art, aware of the **evidence** in the present application, would expect that vinyl chloride and vinylidene chloride would exhibit "similar behavior when reacted with HF" since the **evidence** shows that they behave differently when reacted with

HF. Applicants therefore respectfully submit that a person of ordinary skill in the art would not find the subject matter of the rejected claims obvious in view of the cited references. Applicants respectfully request the Examiner to reconsider and withdraw the rejection of the claims under Section 103.

Lovelace discloses the reaction of vinyl chloride with hydrogen fluoride to produce 1-chloro-1-fluoroethane (see page 13). Lovelace indicates that the use of excess hydrogen fluoride may result in 1,1-difluoroethane product. Lovelace also discloses the reaction of vinylidene chloride with hydrogen fluoride to produce 1,1-dichloro-1-fluoroethane, 1-chloro-1,1-difluoroethane, and 1,1,1-trifluoroethane (see the top of page 14). Applicants respectfully submit that Lovelace cannot reasonably be interpreted as disclosing that vinyl chloride **is analogous** that is that it behaves similarly in all respects, to vinylidene chloride in hydrofluorination processes. Applicants respectfully submit that **vinyl chloride is far more reactive than vinylidene chloride**, and thus has a far greater tendency than vinylidene chloride to form heavy by-products by oligomerization.

In response to the Declaration by Janssens, the Examiner states:

[T]he instant rejection is not predicated upon an assumption of analogous reactivity but upon the reasonable expectation that a known useful product would be obtained if vinyl chloride is used in the prior art process.

The present claims do not specify a process for producing **any** "known useful product", but rather specify a process for the manufacture of 1-chloro-1-fluoroethane, 1,1-difluoroethane, or mixtures thereof. Applicants respectfully submit that the **evidence** of record clearly demonstrates that claimed process would not have been obvious to a person of ordinary skill in the art in view of the reference disclosures.

The Board's attention is respectfully directed to the examples in applicants' specification at pages 9 to 14. In particular, the Board's attention is respectfully directed to Examples 1(C) and 4(C) which have been carried out in accordance with the prior well-known processes discussed at pages 1 and 2 of the specification. These examples (all of which are in Appendix 3 to the present Brief) are to be compared with Example 3 (with respect to comparative example 1(C)), and with Example 5 (with respect to comparative example

4(c)). Examples 3 and 5 have been carried out in accordance with the subject matter of claims 1 or 21.

The Board's attention is respectfully directed to Table I at page 14 of the specification. Therein the Board will note that the claimed process (as in Examples 3 and 5) leads to reduced formation of heavy halogen-containing side products (expressed as selectivity on the basis of vinyl chloride converted). Comparing Example 3 to comparative example 1(C), the Board will note that in Example 3 heavy halogen-containing side products constituted 8% whereas in comparative example 1C these heavy halogen-containing side products constituted 35%. Similarly, comparing Examples 5 (according to the invention) with comparative example 4(C), the Board will note that in comparative example 4(C) the heavy halogen-containing side products constituted 25% whereas in Example 5 according to the invention the heavy halogen-containing side products constituted 4%.

When considering all aspects of the chemical principles of the involved reactions (reactivity, thermodynamics, kinetics, etc.), nothing in the prior art discloses or suggests that the claimed process would allow the reduction of formation of heavy halogen-containing side products **by more than four times** in the specified chemical reaction. Applicants respectfully submit

that the evidence of record clearly demonstrates the unobvious nature of the claimed invention.

With respect to chemical reactions as discussed above, applicants respectfully submit that logically, increasing the concentration of 1-chloro-1-fluoroethane, 1,1-difluoroethane and/or 1,1-dichloroethane, the preferred solvents used in the claimed process, would increase the concentration of vinyl chloride in the reaction medium. As vinyl chloride is the precursor of the heavy halogen-containing side products, a person of ordinary skill in the art (not aware of applicants' invention) would expect that there would be **an increase** in the formation of these heavy halogen-containing side products. In fact, exactly the opposite effect is observed. Applicants respectfully submit that clearly a person of ordinary skill in the art would not have found the claimed invention obvious from the reference disclosures.

CONCLUSION

For the reasons discussed above, applicants respectfully request the Honorable Board of Patent Appeals and Interferences to review and reverse the rejection of their claims under Section 103.

Respectfully submitted,



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APPENDIX 1
CLAIMS ON APPEAL

1. A process for the manufacture of 1-chloro-1-fluoroethane, 1,1-difluoroethane or mixtures thereof, with reduced formation of heavy halogen-containing side products, by reaction between hydrogen fluoride and vinyl chloride in the liquid phase, wherein the hydrogen fluoride and the vinyl chloride are introduced into an organic solvent consisting of at least one saturated halogen-containing hydrocarbon.

2. The process according to Claim 1, wherein the saturated halogen-containing hydrocarbon is selected from chloro-, fluoro- or chlorofluorohydrocarbons containing from 1 to 8 carbon atoms.

3. The process according to Claim 2, wherein the saturated halogen-containing hydrocarbon of the process is used as solvent.

4. The process according to Claim 1, wherein the reaction mixture contains, at all times, at least 55% by weight of solvent.

5. The process according to Claim 1, wherein the introduction of the vinyl chloride and hydrogen fluoride is controlled so that, at all times, the vinyl chloride content is less than 15% and that of hydrogen fluoride is less than 30% of the weight of the reaction mixture.

6. The process according to Claim 1, wherein the molar ratio between the hydrogen fluoride and the vinyl chloride used is at least 1 and does not exceed 20.

7. The process according to Claim 1, wherein the reaction is carried out in the presence of a hydrofluorination catalyst chosen from derivatives of metals of groups IIIa, IVa, IVb, Va, Vb and VIb of the Periodic Table of the elements, and their mixtures.

8. The process according to Claim 1, wherein the reaction is performed at a temperature of at least 40° and not exceeding 130°C and at a pressure at least equal to 2 bar and not exceeding 50 bar.

9. The process according to Claim 1, wherein the product is withdrawn continuously from the reaction mixture.

10. The process according to Claim 9, wherein the product is 1,1-difluoroethane, which is withdrawn in gaseous form.

11. A process for the manufacture of 1-chloro-1-fluoroethane, 1,1-difluoroethane or mixtures thereof comprising:

reacting hydrogen fluoride and vinyl chloride in an organic solvent consisting of at least one saturated halogen-containing hydrocarbon selected from the group consisting of 1-chloro-1-fluoroethane, 1,1-difluoroethane, 1,1-dichloroethane and 1,3-dichloro-1-fluorobutane and

recovering 1-chloro-1-fluoroethane, 1,1-difluoroethane, or mixtures thereof.

12. The process according to claim 11, wherein the reaction mixture contains, at all times, at least 55% by weight of solvent.

13. The process according to claim 11, wherein the introduction of vinyl chloride and hydrogen fluoride is controlled so that, at all times, vinyl chloride content is less than 15% and hydrogen fluoride content is less than 30% of the weight of the reaction mixture.

14. The process according to claim 11, wherein the molar ratio between hydrogen fluoride and vinyl chloride is at least 1 and does not exceed 20.

15. The process according to claim 11, wherein the reaction is carried out in the presence of a hydrofluorination catalyst chosen from derivatives of metals of groups IIIa, IVa, IVb, Va, Vb, and VIb of the Periodic Table of the elements, and mixtures thereof.

16. The process according to claim 11, wherein the reaction is performed at a temperature of at least 40°C and not exceed 130°C and at a pressure equal to 2 bar and not exceeding 50 bar.

17. The process according to claim 11, wherein a desired product is continuously recovered.

18. The process according to claim 17, wherein said product is 1,1-difluoroethane, withdrawn in gaseous form.

19. The process according to claim 1, wherein said reaction is at a temperature between 80° and 110°C.

20. The process according to claim 11, wherein said reaction is at a temperature between 80° and 110°C.

21. A process for the manufacture of 1-chloro-1-fluoroethane, 1,1-difluoroethane, or mixtures thereof, with reduced formation of heavy halogen-containing side products, by contacting hydrogen fluoride and vinyl chloride in a reaction mixture under such conditions that the vinyl chloride content is maintained in the reaction mixture at less than 15% by weight.

22. The process according to Claim 21, wherein said vinyl chloride content is at least 0.1% by weight.

23. The process according to Claim 21, wherein said vinyl chloride content is at least equal to 0.5% by weight and less than 10% by weight.

24. The process according to Claim 21, wherein said reaction mixture contains less than 30% by weight of hydrogen fluoride.

25. The process according to Claim 21, wherein the molar ratio between hydrogen fluoride and the vinyl chloride is at least 1 and does not exceed 20.

26. The process according to Claim 21, wherein the reaction is carried out in the presence of a hydrofluorination catalyst selected from the group consisting of derivatives of metals of Groups IIIa, IVa, IVb, Va, Vb, and VIb of the Periodic Table of the Elements, and their mixtures.

27. The process according to Claim 21, wherein the reaction is performed at a temperature of at least 40° C and not exceeding 130° C and at a pressure at least equal to 2 bar and not exceeding 50 bar.

28. The process according to Claim 21, wherein a desired product selected from group consisting of 1-chloro-1-1 fluoroethane, 1,1-difluoroethane, and mixtures thereof is withdrawn continuously from the reaction mixture.

29. The process according to Claim 28, wherein said desired product is 1,1-difluoroethane in gaseous form.

APPENDIX 2



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Group Art Unit:- 1206

Examiner: Mr. Alan M. Siegel

In re PATENT APPLICATION of:

Applicants : Pascal PENNETREAU et al.)

Application No.: 08/285,015)

Filed : August 2, 1994)

For : PROCESS FOR THE)
 PREPARATION OF 1-CHLORO-)
 FLUOROETHANE AND/OR)
 1,1-DIFLUOROETHANE)

DECLARATION
 UNDER 37 CFR
 1.132

Attorney Docket: SLVAY 0829)

Honorable Commissioner of Patents and Trademarks
 Washington, D.C. 20231

Sir:

Now comes Francine JANSSENS, a co-inventor of the
 above-identified application, who DECLARES:

That she is fully familiar with the invention described
 in the above-identified patent application and the Official
 Action dated November 17, 1994;

To further establish the very different reactivities of
 vinyl chloride and vinylidene chloride, she has conducted the
 following tests, using vinylidene chloride as starting
 material, in conditions similar to those of Examples 1 and 4
 at pages 9 to 11 of the above-identified patent
 specification;

In the test carried out with vinyl chloride (VC) in the
 absence of catalyst, reported in Example 1 of the present

application, more than 95% of VC was converted after 1 hour of reaction. Selectivities were 59% of 1-chloro-1-fluoroethane (151a), less than 1% of 1,1-dichloroethane (152a), ~~5~~ ^{fluoro} % of 1,1-dichloroethane (11DCE) and 35% of heavies. It can be added that a complete VC conversion is obtained after 2 hours.

In a test carried out with vinylidene chloride (VC2) in conditions similar to those of Example 1, 6 hours of reaction were needed to reach a 99% VC2 conversion. Selectivities were 91% of 1,1-dichloro-1-fluoroethane and only 5% of heavies.

In the test carried out with vinyl chloride (VC) in the presence of a catalyst, reported in Example 4 of the present application, selectivities were 12% of 1-chloro-1-fluoroethane (151a), 4% of 1,1-dichloroethane (152a), 59% of 1,1-dichloroethane (11DCE) and 25% of heavies.

In a test carried out with vinylidene chloride (VC2) in conditions similar to those of Example 4, selectivities were 54% of 1,1-dichloro-1-fluoroethane, 41% of 1-chloro-1,1-difluoroethane and only 0.7% of heavies. Example 1(R) of Walraevens et al. (column 5, lines 15-64) reports very similar results obtained in analogous conditions.

The comparison of these additional examples with Examples 1 and 4 of the present application clearly evidences that, in similar conditions:

- (1) vinyl chloride is highly more reactive than vinylidene chloride;
- (2) more "heavies" are formed in a system starting from vinyl chloride than from vinylidene chloride;
- (3) parallel reactions with ClH are far more important in a system starting from vinyl chloride (production of 1,1-dichloroethane) than in the system starting from vinylidene chloride (very limited formation of 1,1,1-trichloroethane).

Declarant therefore respectfully submits that it is clear that the reactivity of vinyl chlorides is not analogous to the reactivity of vinylidene chloride, and that the products obtained when vinylidene chloride is replaced by vinyl chloride in a given process are not necessarily those in which a fluorine group replaces one chloro group, as asserted by the Examiner. Declarant also respectfully submits that in view of the above experiments, there is no reasonable expectation of obtaining a known useful product with high selectivity when replacing the vinylidene chloride starting material by vinyl chloride, and thus a person of ordinary skill in the art would have had no motivation to make the modifications suggested by the Examiner. Furthermore, the process of claim 11, using solvents not even

disclosed by Walraevens, could not possibly have been obvious in view of the Walraevens disclosure.

I declare, as provided by Title 28, United States Code, Section 1746, (Manual of Patent Examining Procedure, Section 602) under penalty of perjury under the laws of the United States of America that the foregoing is true and correct.

Executed this 14 day of March, 1995.

Francine Janssens
Francine JANSSENS

3 corrections ~~if~~
on p. 2

APPENDIX 3

in the vapour state. On account of the presence of the organic solvent, the vinyl chloride may be introduced into the reactor even in the liquid state without bringing about the formation of large amounts of heavy side products. The process according to the invention has the great advantage of a production efficiency which is far superior to that which is possible by the known prior process in which the vinyl chloride is introduced in gaseous form into a liquid medium essentially consisting of hydrogen fluoride, while limiting the formation of heavy side products. It allows excellent selectivities and yields of 1-chloro-1-fluoroethane and 1,1-difluoroethane to be obtained, which are much superior to those obtained in the known prior processes. In addition, depending on the reaction conditions used and the nature of the catalyst which is optionally used, it allows a wide range of variation in the quantitative ratio between the 1-chloro-1-fluoroethane and the 1,1-difluoroethane formed.

The examples which follow are given with the aim of illustrating the invention, but are in no way limiting.

Example 1 (Comparison)

After having been placed under vacuum and cooled to -20°C , a stainless steel autoclave of capacity 0.5 l, fitted with a stirrer, a temperature probe, a descending tube allowing samples in liquid phase to be taken and an inlet for introduction of the reactants, was successively loaded with 127 g of liquid vinyl chloride (VC), and then with 84 g of liquid hydrogen fluoride (HF), so as to obtain an HF / VC molar ratio equal to 2. The autoclave was subsequently immersed in an oil bath preheated to a suitable temperature, so as to bring the liquid reaction mixture, which is kept stirring, to a temperature of 60°C . The reaction mixture was maintained at this temperature under autogenous pressure for one hour. The main operating conditions and the results of analysis by gas chromatography (GC) of a sample taken from the liquid reaction mixture are collated in Table I. The column

"Conv. VC" expresses the degree of conversion of VC, that is to say the amount of VC converted relative to the amount of VC used. For the various products formed (151a = 1-chloro-1-fluoroethane; 152a = 1,1-difluoroethane; 11DCE = 1,1-dichloroethane; heavy = heavy side products), the selectivity corresponds to the amount of VC converted into this product relative to the total amount of VC converted. This example shows that, under the conditions of Patent DE 859,887, that is to say with an initial VC content in the reaction mixture equal to 100 mol% of the organic compounds, heavy side products are formed in very large amounts.

Example 2 (Comparison)

A test was performed at 30°C, in the same apparatus as that used in Example 1, starting with a liquid reaction mixture consisting exclusively of VC and HF, with an HF / VC molar ratio of 50. The results obtained after one hour at 30°C are presented in Table I. This example shows that, in the absence of saturated halogen-containing hydrocarbon in the initial liquid reaction mixture, the use of a very large excess of hydrogen fluoride does not prevent the conversion of a large fraction of the VC to heavy side products.

Example 3 (in accordance with the invention)

A test was performed at 60°C, in the same apparatus as that used in the above examples, starting from a liquid reaction mixture consisting of VC, 1,1-dichloroethane and HF, with an HF / VC / 11DCE molar ratio of 10/1/10. The results obtained after 2 hours at 60°C are presented in Table I. By comparison with Examples 1 and 2, Example 3 according to the invention shows that, when the reactants are diluted in a halogen-containing hydrocarbon from the start of the process, the amount of heavy side products formed is greatly reduced. In addition, this example shows that, in the absence of catalyst, a very high selectivity of 1-chloro-1-fluoroethane is obtained.

Example 4 (Comparison)

A test was performed at 60°C, in the same

apparatus as that used in the above examples, starting from a liquid reaction mixture consisting of VC and HF, with an HF / VC molar ratio of 3/1, in the presence of 0.05 mol of SnCl₄ per mole of VC. The results obtained after reaction for 2 hours at 60°C are presented in Table I. This example shows that, under similar conditions to those of US Patent 2,495,407, that is to say with an initial VC content in the liquid reaction mixture equal to 100 mol% of the organic compounds and in the presence of SnCl₄ as catalyst, heavy side products are formed in very large amounts.

Example 5 (in accordance with the invention)

The test of Example 4 was repeated in the presence of 1,2-dichloroethane (12DCE) as halogen-containing hydrocarbon (HF / VC / 12DCE molar ratio = 12/1/9). At the start, the reaction leads mainly to the formation of HFA-151a (close to 80% selectivity for the first few minutes). The content of HFA-151a subsequently decreases in favour of the formation of HFA-152a. Heavy formation remains limited. After reaction for 4 hours, the conversion of VC is complete. The results obtained after reaction for 4 hours at 60°C are presented in Table I.

Examples 6 to 12 (in accordance with the invention)

A series of tests was performed at 80°C, in the same apparatus as that used in the above examples, starting from a liquid reaction mixture consisting of VC, HF, 1,2-dichloroethane as halogen-containing hydrocarbon and various hydrofluorination catalysts. The detailed operating conditions and the results are collated in Table I. These examples illustrate the influence of the nature of the catalyst on the quantitative distribution of the products obtained. In the absence of the catalyst or in the presence of vanadium tetrafluoride, chromium trifluoride or vanadium trichloride, the main product formed is 1-chloro-1-fluoroethane. In the presence of tin tetrachloride, molybdenum pentachloride or tungsten hexachloride, larger amounts of 1,1-difluoroethane are formed. In all cases, the amount of heavy side products remains low. Depending on the catalyst used, the process

thus allows a wide range of variation in the ratio between the 1-chloro-1-fluoroethane and 1,1-difluoroethane formed.

Examples 13 and 14 (in accordance with the invention)

5 The test of Example 5 was repeated in the presence of various amounts of tin tetrachloride. The results obtained after reaction for 4 hours at 60°C are presented in Table I. In the test of Example 14, after 6
10 hours at 60°C, the temperature of the reactor was subsequently brought to 80°C. After 1 hour at this temperature, the distribution of the products was as follows: HFA-151a : 10%; HFA-152a : 65%; 11DCE : 16%; heavy side products: 9%. Comparison of these examples with Examples
15 5 and 11 teaches that it is also possible to vary the distribution between the resulting 1-chloro-1-fluoroethane and 1,1-difluoroethane by adjusting the amount of catalyst in the solvent and/or the temperature. The amount of 1,1-difluoroethane formed increases to the detriment of the amount of 1-chloro-1-fluoroethane formed
20 when the amount of catalyst increases or when the temperature increases, without resulting in a large variation in the amount of heavy side products formed.

Examples 15-19 (in accordance with the invention)

25 The following tests were performed continuously, at a temperature of 90°C and at a pressure of 15 bar, in a 200 cm³ stainless steel reactor fitted with a stirrer, a jacket in which an oil for heating the reactor circulates and an overflow tube for withdrawal, maintained at the same temperature as the reactor. The vinyl chloride,
30 hydrogen fluoride and catalyst were introduced continuously into the reactor, initially containing 1-chloro-1-fluoroethane as halogen-containing hydrocarbon, maintained in liquid form at the reaction temperature by controlling the pressure in the reactor. After 5 hours of
35 establishment of the conditions, samples of the gaseous phase and of the liquid phase overflowing from the autoclave were taken. After returning to atmospheric pressure and neutralizing in 0.1 molar caustic washing scrubber, the effluent was analysed by gas

chromatography. The operating conditions and the results obtained are given in Table II. Examples 15 to 19 show the very particular advantage of performing the process according to the invention continuously, in particular for drastically limiting the formation of heavy side products. In addition, comparison of the results of Examples 15 and 16 shows that the amount of 1,1-difluoroethane formed increases to the detriment of 1-chloro-1-fluoroethane as the residence time increases. Comparison of the results of Examples 15 and 17 shows the same effect as the catalyst concentration increases. Comparison of the results of Examples 15 and 18, on the one hand, and of Examples 16 and 19, on the other hand, shows the same effect as the HF/VC ratio increases. In no case does a modification of these parameters result in a large variation in the amount of heavy side products formed.

TABLE I

Ex.	Composition of the reaction mixt. (HF/VC/EC*) (mol. ratio)	Catalyst (mole/mol VC)	Control temp. (°C)	Time at stable temp (h)	Conv. VC (%)	Selectivities (% VC converted)			
						151a	152a	11DCE	Heavy
1(C)	2 / 1 / 0	-	60	1	95	59	< 1	5	35
2(C)	50 / 1 / 0	-	30	1	97	50	< 1	4	46
3	10 / 1 / 10	-	60	2	89	91	< 1	nm*	8
4(C)	3 / 1 / 0	0.05 SnCl ₄	60	2	100	12	4	59	25
5	12 / 1 / 9	0.05 SnCl ₄	60	4	100	40	15	41	4
6	11 / 1 / 8	-	80	2	99	84	2	2	12
7	9 / 1 / 9	0.05 VF ₄	80	1	99	89	1	2	8
8	11 / 1 / 9	0.05 CrF ₃	80	2	99	89	1	2	8
9	11 / 1 / 9	0.05 VCl ₃	80	2	99	88	1	3	8
10	12 / 1 / 10	0.05 WCl ₅	80	4	100	48	11	28	13
11	12 / 1 / 10	0.05 SnCl ₄	80	4	100	23	33	33	11
12	12 / 1 / 10	0.05 MoCl ₅	80	4	100	28	27	38	7
13	12 / 1 / 9	0.01 SnCl ₄	60	4	100	70	6	12	12
14	11 / 1 / 9	0.24 SnCl ₄	60	4	100	21	34	40	5

* : EC = saturated halogen-containing hydrocarbon

* : nm = not measured

TABLE II

Ex. No.	Residence time (h)	HF/VC/SnCl ₄ Ratio (mol/mol/mol)	Conversion VC (%)	Selectivities (% VC converted)				152a/151a Ratio
				151a	152a	11DCE	Heavy	
15	1	2.8/1/0.007	99.3	29	52	16	0.9	1.79:1
16	0.38	2.5/1/0.007	92	43	42	14	0.4	0.98:1
17	1	3/1/0.003	99.6	42	31	26	1.2	0.74:1
18	1	1.6/1/0.007	99.4	47	30	21	1.8	0.64:1
19	0.38	6.2/1/0.007	99.7	24	65	10	0.9	2.71:1